Indian J. Phys. 43, 177–183 (1969)

Molecular constants of a few Group IV tetra hydrides and their deuterium substituents

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(*Received October* 22, 1968 ; *Resubmitted January* 15, 1969)

The potential energy constants of a few Group IV tetrahydrides belonging to the tetrahedral XY_4 type were obtained by the method of "Characteristic set" of vibrational symmetry co-ordinates. The values were determined without any assumption regarding any specific force field. The mean amplitudes of vibration for the various characteristic bonds were determined by Cyvin's method. The Coriolis coupling constants and the rotational distortion constants were also obtained, which verify the validity of the symmetry force constants obtained by this method.

Introduction

Several attempts have been made earlier, to calculate the potential energy constants which help in the thorough understanding of the molecular dynamics. But it is not always possible to calculate the force constants from the vibrational spectral data alone, since the number of force constants exceed the number of fundamental frequencies. So one is forced to assume some specific force field as in the case of UBFF (Urey & Bradley 1931), HBFF (King 1962) and OVFF (Heath & Linnett 1948) or turn to other data regarding other molecular constants, and such attempts have been made previously by several workers (Aldous & Mills 1962, 1964 ; Krishna Pillai & Perumal 1964 ; Duncan & Mills, 1964). One such attempt in this direction has been made by Herranz & Castano (1966). This method does not make any specific assumption regarding force fields. Herranz & Castano (1966) have already applied this method to calculate the potential constants of silane and deutero-silane. In the present study we have applied their method for the calculation of all the molecular constants of Group IV tetrahydrides and their deuterium substituents.

Potential energy constants.

A set of orthogonal, normalised internal symmetry co-ordinates (Cyvin 1960) was used in the normal co-ordinate analysis. As suggested by Herranz & Castano (1966), "a characteristic set" of symmetry co-ordinates is the one for which the trace of the matrix of transformation between symmetry and normal co-ordinate (L), is maximum. Such a matrix provides the most, or one close to the most, physically significant set of valence symmetary co-ordinates for use in assigning all the normal co-ordinates of the molecule.

It is well known that (Wilson *et al* 1965),

$$F = \overset{*}{L}^{-1}\Lambda L^{-1} \qquad \ldots(1)$$

and

$$G = L\overset{*}{L} \qquad \ldots(2)$$

where F and G are Wilson's potential and inverse kinetic energy matrices and Λ is the diagonal matrix whose elements,

$$\Lambda_k = 4\pi^2 C^2 \nu_k^2 \qquad \ldots(3)$$

are arranged according to the frequency assignments previously made (ν_k is the vibrational frequency in cm^{-1} of the k^{th} mode and C is the velocity of light).

The orthogonal matrix B, which diagonalizes G was constructed as suggested by Herranz & Castano (1966) from which,

$$L^{-1} = BM^{1/2}\overset{*}{B} \qquad \ldots(4)$$

where $M^{1/2}$ is the diagonal matrix of the reciprocal of the positive square root of the eigenvalues of G. The asterisk denotes the transposition of a matrix.

It is seen from the above relations, that by choosing a set of co-ordinates which will be characteristic of the normal modes of vibration, it is possible to compute L^{-1} directly from G matrix which depends on the geometry of the molecule alone.

Hence one can determine the symmetry force constants (F) without any ambiguity. To check the exactness of the choice of the characteristic set of symmetry co-ordinates, the potential energy distribution for the various normal modes in the different cases are calculated from the relation of Morino & Kuchitsu (1952),

$$X_{ik} = F_{ii}\frac{L_{ik}^2}{\lambda_k} \qquad \ldots(5)$$

where X_{ik} is the potential energy distribution of the i^{th} symmetry co-ordinate to the k^{th} normal mode and L_{ik} is the ik^{th} element of the L matrix.

The set of the orthonormalised internal symmetry co-ordinates chosen for the tetrahedral XY_4 type molecules are the same as those used by Cyvin (1960). The G matrix elements were obtained by the usual procedure and the symmetry force constants were obtained from (1) and (4). The computed F elements along with the values reported by Herranz & Castano (1966) for silane and deutero-silane are given in table 1.

TABLE 1. SYMMETRY FORCE CONSTANTS† OF A FEW GROUP IV TETRAHYDRIDES AND THEIR DEUTERATED DERIVATIVES

F elements.	CH_4	SiH_4	GeH_4	CD_4	SiD_4	GeD_4
F_{11}	5.0045*	2.7999	2.3323	5.1268	2.8190	2.6645
F_{22}	0.5586	0.4052	0.3176	0.5665	0.4088	0.4049
F_{33}	4.6098	2.6994 (2.729)	2.6210	5.1685	2 7608 (2.796)	2.4358
F_{44}	0.5162	0.5025 (0.500)	0.4370	0.5599	0.5112 (0.521)	0.5004
F_{34}	0.2886	0.0759 (-0.117)	0.0254	0.5859	0 1444 (-0 223)	0 0799

†Unit used mdyn/A.

*This number of significant figures are retained for internal consistency in the calculations.

Note: Data used in these calculations are the same as those used in a previous paper by the authors (Ramaswamy & Ranganathan, 1968).
The values in parenthesis are those reported by Herranz & Castano (1966).

The potential energy distributions for the various modes evaluated using equation (5) are presented in table 2.

TABLE 2. POTENTIAL ENERGY DISTRIBUTION FOR THE GROUP IV TETRAHYDRIDES AND THEIR DEUTERIDES FOR THE f_2 SPECIES

Sym. coord.	CH_4 Q_3	Q_4	SiH_4 Q_3	Q_4	GeH_4 Q_3	Q_4
S_3	1.008499*	0.003114	1.001205	0.003101	1.000141	0.000420
S_4	0.005205	1.035658	0.000101	1.018959	0.000011	1.000552
	CD_4 Q_3	Q_4	SiD_4 Q_3	Q_4	GeD_4 Q_3	Q_4
S_3	1.030543*	0.104057	1.004237	0.010728	0.995848	0.003757
S_4	0.002191	1.132408	0.000361	1.014664	0.000118	1 005141

*This number of significant figures are retained for internal consistency in the calculations.

MEAN SQUARE AMPLITUDES OF VIBRATION

The elements of the mean square amplitude matrix were evaluated by the method suggested by Cyvin (1959). The relation is ginen by,

$$\Sigma = L\Delta\tilde{L} \qquad \ldots(6)$$

where Δ is a diagonal matrix whose elements are defined as,

$$\Delta_k = \frac{h}{8\pi^2 \nu_k C} \coth\left(\frac{h\nu_k C}{2kT}\right) \qquad \ldots(7)$$

where h is Planck's constant, k Boltzmann's constant, T is absolute temperature and C is the velocity of light in vaccum. All the calculations were made for 298.16°K and the results are presented in table 3.

TABLE 3. SYMMETRIZED MATRIX ELEMENTS FOR GROUP IV TETRA HYDRIDES AND THEIR DEUTERIDES

Σ Elements.	CH_4	SiH_4	GeH_4	CD_4	SiD_4	FeD_4
Σ_{11}	0.005735*	0.007669	0 008402	0.004013	0.005343*	0.005496
Σ_{33}	0.027263	0.024206	0.026980	0.019304	0.017980	0.017658
Σ_{22}	0.006633	0.008184	0.008000	0 004672	0.005840	0.006190
Σ_{44}	0.026125	0.018944	0.019344	0.021171	0.014736	0.013298
Σ_{34}	−0.001902	0.000639	−0 000225	- 0 002646	−0.000908	−0.000517

*This number of significant figures are retained for internal consistency in the calculations.

TABLE 4. CORIOLIS COUPLING CONSTANTS OF GROUP IV TETRA HYDRIDES AND THEIR DEUTERIUM ANALOGUES

Coriolis constants	CH_4 Cal. Present	CH_4 Shimanouchi *et al* (1966) Obs.	CH_4 Shimanouchi *et al* (1966) Cal	SiH_4 Cal present	SiH_4 Shimanouchi *et al* (1966) Obs.	SiH_4 Shimanouchi *et al* (1966) Cal.	GeH_4 Present	CD_4 Present	SiD_4 Present	GeD_4 Present
ζ_{33}	0.081	0.056	0 036 0 071	0.027	0.046	0.033	0.002	(0.222)	(0.109)	(0.050)
ζ_{34}	0.419	0.450	0.464 0.429	0.454	0.454	0.467	0.498	(0.279)	(0.391)	(0.450)

The values in parentheses are those obtained using the force constants of their hydrogenated molecule.

Coriolis coupling constants

The Coriolis coupling constants are determined from the two equations.

$$Tr|F(G-C)| = Tr|\lambda\,(E-Z)| \quad .. (8)$$

and

$$\zeta_3 + \zeta_4 = 0.5 \quad .. (9)$$

where C is a matrix as defined by Shimanouchi *et al* (1966). The ζ values have been tabulated.

Rotational distortion constants

Following the procedure of Kivelson & Wilson (1952, 1953), the derivatives of the moments of inertia tensor with respect to the various internal co-ordinates defined as J^is were constructed and the different $\tau_{\alpha\beta\gamma\delta}$ elements were determined which are defined as,

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2}\, I^{\circ}_{\alpha\alpha}\, I^{\circ}_{\beta\beta}\, I^{\circ}_{\gamma\gamma}\, I^{\circ}_{\delta\delta} \sum_{ij}^{n} J^i_{\alpha\beta}\,(F^{-1})_{ij}\, J^j_{\gamma\delta} \quad .. (10)$$

where α, β, γ, δ can take in turn x, y, or z, I° are the components of the moment of inertia tensor and i refers to the internal co-ordinate. The rotational distortion constants D_J and D_{JK} for the various Group IV tetrahydrides and deuterides are given in table 5.

Table 5. Rotational distortion constants of Group IV tetrahydrides and their deuterium substitutents

(in mc/sec.)

Rotational distortion constants.	CH_4	SiH_4	GeH_4	CD_4	SiD_4	GeD_4
D_J	3 420	1.203	1.116	0.812	0.281	0.229
D_{JK}	0.657	0.459	0.638	0.363	0.160	0.196

Discussion of results

The method suggested by Herranz has been successfully applied to the case of Group IV tetrahydrides and their deuterium substituted derivatives. The *X-H* stretching force constants obtained as 4.945 md/Å for C-H, 2.725 md/Å for Si-H and 2.549 md/Å for Ge-H are in good agreement with the values obtained by Mills (Mansel Davies, 1963). The increase in the C-D and Si-D stretching force constants can be attributed to some shrinkage effect of the *X-D* bond. The variation of the interaction constants obtained here are consistent with the results obtained earlier.

(Linnett & Wheatley 1949) and (Mills 1960). The bending force constants are also in agreement with the expected results. The symmetry force constants of silane and deuterosilane obtained by the present calculations are compared with the calculated values of Herranz & Castano (1966). The differences in the interaction constants may be due to the differences in the choice of the characteristic set of symmetry coordinates by the present authors and by Herranz & Castano (1966).

The C-H and H-H mean amplitudes of vibration obtained as 0.08005Å and 0.11984Å and the corresponding C-D values of 0.06714Å and 0.09348A° are in good agreement with the electron diffraction results of Bartell *et al* (1961). The values of Si-H, Ge-H, Si-D and Ge-D mean amplitudes obtained as 0.08975Å for Si-H, 0 09000Å for Ge-H, 0.07560 for Si-D and 0.07757Å for Ge-D agree well with the earlier calculations of Venkateswarlu & Rajalakshmi (1965). The non bonded interaction of H-H and D-D values of 0.126448Å in SiH_4, 0.130769Å in GeH_4 0.106320 in SiD_4 and 0.107815Å in GeD_4 also agree with the results of the earlier workers (Venkateswarlu & Rajalakshmi 1966). All the above reported values are in good agreement with the values obtained using Green's Function procedure also (Ramaswamy & Ranganathan 1968).

The nature of the potential energy distribution between the two triply degenerate modes suggests the purity of the modes chosen and that the mixing between them is very negligible.

The individual values of the Coriolis coupling constants have been determined assuming the Coriolis sum rule which has been readily verified by the authors elsewhere (Ramaswamy & Ranganathan 1968). The values of the Coriolis coupling constants agree well with the values reported by earlier workers (Shimanouchi *et al* 1966). The rotational distortion constants are also very close to the values of the earlier calculation (Shimanouchi *et al* 1966, Thyagarajan & Herranz 1961 and Ramaswamy & Ranganathan 1968).

Conclusion

The determination of an unambiguous set of potential constants and other molecular constants have been well facilitated by the method suggested by Herranz & Castano. This has been successfully applied in the case of a few Group IV tetrahydrides and their deuterated derivatives which proves the applicability of the method here.

One of the authors (V. R.) is thankful to the Council of Scientific and Industrial Research, Government of India, New Delhi for the award of a Junior Research Fellowship.

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